Improving the efficiency of water splitting in dye-sensitized solar cells by using a biomimetic electron transfer mediator

Yixin Zhao1, John R. Swierk1, Jackson D. Megiatto Jr2, Benjamin Sherman3, W. Justin Youngblood3, Dongdong Qin4, Deanna M. Lentz2, Ana L. Moore4, Thomas A. Moore4, Devens Gust4, and Thomas E. Mallouk1,4

1Department of Chemistry, The Pennsylvania State University, University Park, PA 16802; 2Department of Chemistry and Biochemistry and Center for Bioinspired Solar Fuel Production, Arizona State University, Tempe, AZ 85287; and 3Department of Chemistry, University of North Texas, Denton, TX 76203

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Photoelectrochemical water splitting directly converts solar energy to chemical energy stored in hydrogen, a high energy density fuel. Although water splitting using semiconductor photoelectrodes has been studied for more than 40 years, it has only recently been demonstrated using dye-sensitized electrodes. The quantum yield for water splitting in these dye-based systems has, so far, been very low because the charge recombination reaction is faster than the catalytic four-electron oxidation of water to oxygen. We show here that the quantum yield is more than doubled by incorporating an electron transfer mediator that is mimetic of the tyrosine-histidine mediator in Photosystem II. The mediator molecule is covalently bound to the water oxidation catalyst, a colloidal iridium oxide particle, and is coadsorbed onto a porous titanium dioxide electrode with a Ruthenium polypyridyl sensitizer. As in the natural photosynthetic system, this molecule mediates electron transfer between a relatively slow metal oxide catalyst that oxidizes water on the millisecond timescale and a dye molecule that is oxidized in a fast light-induced electron transfer reaction. The presence of the mediator molecule in the system results in photoelectrochemical water splitting with an internal quantum efficiency of approximately 2.3% using blue light.

artificial photosynthesis | photoelectrochemistry

The design of biomimetic systems for artificial photosynthesis is of fundamental interest in the study of light-driven electron and proton transfer reactions. It also represents a potential route to the efficient conversion of solar energy to energy stored in fuel. System modeling has shown that it should be possible, using complementary dye molecules that absorb in the infrared and the visible, to construct artificial Z-schemes that split water with over 10% energy conversion efficiency (1, 2). It is simpler in many ways to design small molecules with the proper photoredox properties than it is to find a set of semiconductors that can be coupled for visible light water splitting. Nevertheless, the molecular approach has so far lagged behind the semiconductor-based approach where high efficiencies have been realized with expensive materials (3–7).

A ubiquitous problem in molecular artificial photosynthesis is back electron transfer, which rapidly thermalizes the energy stored by light-induced charge separation in donor-acceptor pairs. Recently, our group and several others have studied this problem in dye-sensitized solar cells where a molecular dye and a porous TiO2 electrode act as the donor-acceptor dyad (8–13). The dye is covalently coupled to a colloidal or molecular water oxidation catalyst. Fast back electron transfer, relative to the rate of water oxidation, results in low quantum yields for water splitting in these systems.

It is well known that charge-separation lifetimes in molecular donor-acceptor systems can be increased dramatically by adding secondary electron donors or acceptors to form triads, tetrads, and more complex supermolecules (14). This strategy spatially separates the ultimate donor and acceptor molecules in the chain, and the back electron transfer reaction is slowed because of the exponential dependence of outer-sphere electron transfer rates on distance. Multistep electron transfer is used in many biological systems, including photosynthesis, to control the kinetics of oxidation-reduction reactions. It has been noted that biology prefers to use distance rather than free energy differences to tune electron transfer rates because the former is sufficient and the latter is too expensive in terms of energy efficiency (15).

The four-electron oxidation of water is a kinetically demanding process that occurs on the millisecond timescale in the oxygen-evolving complex (OEC) of Photosystem II as well as in a number of synthetic catalysts (16–20). A key component of Photosystem II is the tyrosine-histidine pair that mediates electron transfer between the OEC and P680*. Synthetic mimics of this biological redox relay have been studied in a number of molecular dyads and triads (21–25). We incorporated a redox mediator into a water-splitting dye-sensitized solar cell (see Scheme 1). Dramatically increased photocurrent is found relative to the simple TiO2-dye-catalyst system. Flash photolysis/transient absorbance measurements show that the mediator accelerates the reduction of the photo-oxidized dye; thus, its function in this system is similar to that of the tyrosine-histidine mediator in Photosystem II.

Results and Discussion

The construction of the electron transport assembly shown in Scheme 1 begins with the synthesis of iridium oxide nanoparticles that are bound to the benzimidazole-phenol (BIP) mediator, and the 2-carboxyethylphosphonic acid (CEPA) anchoring molecule. In earlier papers involving water oxidation using ligand-capped IrOx · nH2O nanoparticles, the nanoparticles were prepared by alkaline hydrolysis of IrCl62− ions in the presence of a carboxylated ligand (11, 26–28). IrOx · nH2O nanoparticles prepared by that method cannot be easily linked to TiO2 photoelectrodes, possibly because relatively few capping ligands coordinate the particle surface under basic conditions. To address this problem, we combined the capping ligands and IrCl62− under slightly acidic conditions (pH 5–6 for 1 h at 80–90 °C) to form the ligand-Ir(IV) complex. Then, we hydroyzed these complexes to form IrOx · nH2O nanoparticles at pH 7–8. CEPA-capped IrOx · nH2O nanoparticles synthesized by this procedure persistently link onto TiO2 nanoparticles (29).


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To whom correspondence should be addressed. Email: tem5@psu.edu.

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photoelectrodes at loadings that can be easily controlled by their concentration and adsorption time.

A second important problem in preparing photoelectrodes catalyzed by IrOx · nH2O nanoparticles is the elimination of the monomeric [Ir(OH)]62− anion that is formed during hydrolysis of IrCl62−. This anion can be detected by its strong absorbance at 310 nm (29–31). Significant dark current and lower photocurrent were observed when TiO2 photoelectrodes or other mesoporous metal oxide photoelectrodes such as Fe2O3 and WO3 were soaked in IrOx · nH2O nanoparticle solutions that contained an [Ir(OH)]62− impurity. We hypothesized that this electroactive anion can access the electrode back contact [a fluorine-doped tin oxide (FTO) film] and, thereby, mediate back electron transfer. The [Ir(OH)]62− impurity can be removed by ion exchange on a DOWEX 1X8-50 resin, and excess free capping ligand in the solution can also be very efficiently removed. For example, free BIP molecules in a solution of BIP and IrOx · nH2O nanoparticles were completely removed after stirring with ion-exchange resin for 1 h. BIP- and CEPA-capped IrOx · nH2O colloids prepared by this method were a deep blue color and had negligible 310 nm absorbance in their UV-vis spectra, which indicates essentially complete conversion of IrCl62− to IrOx · nH2O nanoparticles with negligible [Ir(OH)]62− impurity.

Fig. 1 compares spectra of purified solutions of IrOx · nH2O nanoparticles capped by CEPA, CEPA, and BIP designated 1-IrOx · nH2O and 2-IrOx · nH2O, respectively. There is a broad absorbance centered at 580 nm, which is typical of Iridium (IV) oxide nanoparticles; and, there is no impurity peak at 310 nm present in the 1-IrOx · nH2O spectrum. In addition to the 580 nm peak, the 2-IrOx · nH2O nanoparticles exhibited an absorbance attributed to BIP at 340 nm, which indicates that BIP is covalently bound. Using an extinction coefficient of 18,000 M−1 cm−1 for BIP, the concentration of BIP in the 2-IrOx · nH2O solution is approximately 0.1 mM, and the BIP:Ir mole ratio is approximately 1:10, assuming complete conversion of 1 mM IrCl62− to IrOx · nH2O nanoparticles. In the following discussion, the ratios and concentrations refer to the number of Ir atoms rather than the number of IrOx · nH2O nanoparticles.

TEM images (Fig. 2) show that 1-IrOx · nH2O and 2-IrOx · nH2O consist of irregularly shaped 2-nm nanoparticles. IrOx · nH2O nanoparticles synthesized using other ligands under the same conditions had similar particle sizes and UV-vis absorbance at 580 nm. In contrast, larger IrOx · nH2O aggregates were found if the solution was lower than pH 7 during the hydrolysis, regardless of the type of ligands used. Therefore, it is very important to keep the reaction pH constant at 7–8 during the hydrolysis step to obtain ligand-capped particles without aggregation. The pH of the solution decreases gradually during hydrolysis, and dilute NaOH must be added to maintain a constant pH.

An obvious shortcoming of the coadsorption strategy illustrated in Scheme 1 is that juxtaposition of the sensitizer and BIP-catalyst on the TiO2 surface is uncontrolled. If these components do intimately mix, then changing their ratio should alter the kinetics of the system. In a recent report of photoelectrodes containing a codeposited porphyrin sensitizer and water oxidation catalyst, the ratio of sensitizer to the catalyst, a Cp-Ir complex, was chosen to be 1:1 (10). Previous studies on 2-nm ligand-capped IrOx · nH2O nanoparticles suggest that 20–30% of the Ir atoms should be on the surface (32–34). We experimented in preliminary studies with different molar ratios of the 3P-Ru dye to Ir ranging from 1:1 to 1:10, and we found the highest photocurrents at a 1:5 ratio with 1-IrOx · nH2O or 2-IrOx · nH2O nanoparticles. For consistency, all subsequent electrochemical and transient spectroscopic data were obtained using TiO2 electrodes with 3P-Ru and IrOx · nH2O nanoparticles coadsorbed in molar ratio of 1:5.

The electrocatalytic activity of the 1-IrOx · nH2O or 2-IrOx · nH2O nanoparticles was first assessed by cyclic voltammetry (CV) in the dark in Na2SiF6-NaHCO3 buffer solutions (pH 5.8) shown in Fig. 3. The porous TiO2 electrode itself gives negligible current under these conditions near the water oxidation potential, and an electrode derivatized with the 3P-Ru sensitizer is not catalytic, showing the reversible Ru(II/III) wave only. 1-IrOx · nH2O and 2-IrOx · nH2O nanoparticles deposited on TiO2 photoelectrodes showed significant catalytic current for water oxidation, which was slightly suppressed by coadsorption of 3P-Ru. Although these data establish that the nanoparticles are elec-
trocatalytically active and bound to the electrode, we did not directly observe the oxidation/reduction of the BIP mediator. The (dark) anodic current was lower for electrodes catalyzed by 2-IrO\(_2\) \cdot nH\(_2\)O than by 1-IrO\(_2\) \cdot nH\(_2\)O. Electrochemical characterization of the diethyl ester of BIP (Supporting Information) showed a reversible one-electron oxidation at 1.06 V vs. SCE (+1.10 V vs Ag/AgCl) in acetonitrile.

The photoelectrochemical behavior of 3P-Ru-sensitized electrodes containing 1-IrO\(_2\) \cdot nH\(_2\)O or 2-IrO\(_2\) \cdot nH\(_2\)O under filtered white light illumination is shown in Fig. 4. The 3P-Ru/1-IrO\(_2\) \cdot nH\(_2\)O electrode without the BIP mediator showed an initial photocurrent density of 130 \(\mu\)A/cm\(^2\), which rapidly decayed to a stable photocurrent of 25 \(\mu\)A/cm\(^2\). This steady-state photocurrent is similar to that previously observed using TiO\(_2\) electrodes sensitized with IrO\(_2\) \cdot nH\(_2\)O nanoparticles capped by a heteroleptic Ru Tris(bipyridyl) dye (9, 11). The rapid polarization of the electrode may arise from hole accumulation (as a consequence of the slow kinetics of water oxidation) or the local decrease in pH that arises from the four-electron oxidation of water. The in-

system. In previous experiments on dye-IrO\(_2\) \cdot nH\(_2\)O dyads adsorbed on TiO\(_2\), we observed photoinduced charge injection on a timescale faster (<30 ns) than could be resolved by transient absorption measurements, followed by charge recombination on the timescale of hundreds of microseconds (9, 11). Transient absorbance decays recorded at the absorbance maximum of 3P-Ru, which correspond to charge recombination kinetics in the present system, are shown in Fig. 5. Under both open circuit conditions and at more positive potentials where the photocurrent reaches its maximum value, charge recombination occurs over a broad range of timescales. This is consistent with a trapping/detrapping process for photoinduced electrons. In both cases the kinetics were fit to a stretched exponential distribution, (Eq. 1), with \(\beta\) values in the range of 0.3–0.6.

\[
A(t) = A_0 e^{-t/\tau}\beta + c
\]  

This long-lived component of the decay represented by the constant \(c\) is possibly an artifact of dye desorption at negative potentials under the conditions of the flash photolysis experiments. At open circuit, a very long lifetime component (\(c = 0.15-0.20\) corresponding to 15–20% of the initial transient was needed to fit the data (Fig. 5A). At positive potentials, the data could be adequately fit with \(c = 0.10\) (Fig. 5B).

At both potentials, coadsorption of ligand-capped IrO\(_2\) \cdot nH\(_2\)O particles decreases the lifetime of the Ru(III) form of the sensitizer, which is consistent with electron transfer from Ir(IV) to Ru(III). The lifetime for 3P-Ru dye +1-IrO\(_2\) \cdot nH\(_2\)O at open circuit (0.26 ms) is in good agreement with previous measurements in the TiO\(_2\)-dye/IrO\(_2\) \cdot nH\(_2\)O dyad system (9, 11). Interestingly, incorporation of the BIP mediator molecule decreases \(\tau\) at open circuit and greater positive potentials. Because the distance between the BIP mediator molecules and 3P-Ru dye
**Materials and Methods**

The synthesis of 2-carboxyphosphonic acid (CEPA) Capped IrO\(_x\) \(\cdot\) nH\(_2\)O nanoparticles was conducted by the method previously described (35). TiO\(_2\) films were coated onto fluorine-doped tin oxide-coated glass electrodes (FTO-glass, Hartford, USA, 8 and 15 \(\Omega\) cm\(^2\)) by the doctor-blade method using Scotch tape spacers to adjust the film thickness. The films were then sintered at 450 °C for 30 min. A TiCl\(_4\) treatment was performed following previous reports by soaking the electrodes in 0.05 M TiCl\(_4\) solution at 70 °C for 20 min. The electrodes were annealed at 400 °C for 30 min (36). The TiO\(_2\) photoelectrodes were then connected to insulated copper wires by using silver paste (DuPont 4922N), and the electrical contact was sealed with white epoxy (Hy-sol-C, McMaster-Carr). Electrodes with 7-\(\mu\)m thick TiO\(_2\) films deposited on the 8 \(\Omega\)-cm FTO were used for photoelectrochemical measurements, whereas more transparent photoelectrodes with 4-\(\mu\)m thick TiO\(_2\) films deposited on 15 \(\Omega\)-cm FTO were used for transient UV-vis spectroscopic measurements. The 3P-Ru photoanodes were sensitized using a solution of 3P-Ru dye and IrO\(_x\) \(\cdot\) nH\(_2\)O nanoparticles in different ratios. A typical sensitizer solution was 0.05 mM 3P-Ru dye and 0.25 mM 1- or 2-IrO\(_x\) \(\cdot\) nH\(_2\)O in water. The TiO\(_2\) photoanodes with coadsorbed 3P-Ru dye and IrO\(_x\) \(\cdot\) nH\(_2\)O nanoparticles that were used for photoelectrochemical and transient spectroscopic measurements had absorbance values of 0.8–1.0 and 0.4–0.6 at 464 nm, respectively, relative to a blank FTO reference sample.

**Photoelectrochemical Measurements.** The TiO\(_2\) working electrode was placed in the quartz cuvette of an H-shaped cell with a Pt-wire counter electrode and Ag/AgCl reference electrode in the other compartment of the cell. The entire cell was filled with 37.5 mM Na\(_2\)SiF\(_6\)-NaHCO\(_3\) (1:1.5) silicate buffer (pH 5.8), containing 0.1 M LiClO\(_4\) as the supporting electrolyte and kept under a blanket of Ar gas. The buffer solution was prepared the day prior to the experiment. A 150 W Xe lamp (Ciba-Geigy) was used as the light source with a 410-nm, long-pass filter and a water filter. The photoelectrochemical data were recorded using a digital potentiostat (Bioanalytical Systems 100A).

**Amperometric Detection of O\(_2\) Generated at the Photoanode.** Pt film electrodes were made by sputtering 1 \(\mu\)m thick Pt films onto glass slides with an adhesion layer of Ti and Au. The Pt film electrodes were connected to an insulated Cu wire with silver paste or by soldering and were sealed with white epoxy (Hyso-C, McMaster-Carr) covering the electrical contact. A 1.5-mm thick layer of epoxy was applied to the outer edge of the Pt electrodes as a spacer. Before each measurement, the Pt electrodes were electrochemically cleaned by the following procedure: the electrode was anodized at 1.5 V vs Ag/AgCl for 20 s in 0.5 M H\(_2\)SO\(_4\), then the Pt electrode was continuously cycled between −0.3 V and 1.1 V vs Ag/AgCl at 50 mV/s in 0.5 M H\(_2\)SO\(_4\). The peaks of hydrogen adsorption and stripping became pronounced. The cathodic current corresponding to reduction of dissolved O\(_2\) was measured on a Pine Bipotentiostat (model AFCBP1) using the setup described in our previous study (9).

**Transient Spectroscopy.** Transient absorption measurements were carried out using TiCl\(_4\)-treated, 4-\(\mu\)m thick TiO\(_2\) electrodes. Different components of the electron transfer system, 3P-Ru dye, 3P-Ru dye, 1-IrO\(_x\) \(\cdot\) nH\(_2\)O 3P-Ru dye, and 2-IrO\(_x\) \(\cdot\) nH\(_2\)O nanoparticles, were adsorbed as described above, and the working electrode was held at open circuit (by disconnecting the electrodes and purging with Ar for 15 min) and at −100 mV vs AgCl/Ag by using a
potentiostat as described above. The electrodes were irradiated with a 300 W Xe arc lamp as the analyzing light and photoexcited with a 532-nm Nd:YAG Spectra-Physics INDI laser (200 mJ/pulse, 7 ns). A mechanical shutter minimized exposure of the samples to the white analyzing light. A Spectral Products CM110 monochromator was placed between the Xe lamp and the sample. The analyzing light then passed through the sample and a monochromator (Spectral Products, CM110) and reached a photodiode detector (Thor Labs). Two laser line filters were placed in the beam path before the photodiode to eliminate scattered laser light. Each kinetic trace was recorded by using a Tektronix oscilloscope (TDS 540A) and approximately five shots were averaged to minimize photodegradation.

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Supporting Information

Zhao et al. 10.1073/pnas.1118339109

SI Materials and Methods.
All chemicals were purchased from Aldrich, Alfa Aesar and Acros, and they were used without further purification. Solvents were obtained from EM Science, and they were used as received unless otherwise noted. Thin layer chromatography (TLC) was performed with silica gel coated glass plates from Analtech. Column chromatography, and it was carried out using Silicycle silica gel 60 with 230–400 mesh.

Spectroscopic Measurements. $^1$H NMR spectra were recorded on a Varian spectrometer at 400 MHz or 500 MHz. NMR samples were prepared in deuterated solvents with tetramethylsilane as an internal reference using a Wilmad 528-PP 5 mm NMR tube. Mass spectra were obtained with a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF) using cyano-4-hydroxycinamic acid (CCA) as a matrix. The reported mass is of the most abundant isotopic ratio observed.

Synthesis of the 3P-Ru Dye. This compound was synthesized in six steps as shown in Scheme S1.

**Compound 1.** 2-Acetylpyridine (12.1 g, 0.1 mol) was added to 150 mL MeOH with stirring followed by addition of 40 mL of 1 M NaOH. 4-bromobenzaldehyde (18.5 g, 0.1 mol) was added to the solution with stirring. After 1 h, the precipitate was collected and crystallized with MeOH. The yield was 38%.

**Compound 2.** α,β-unsaturated ketone 1 (15.89 g, 55.2 mmol) was added to a 500 mL round-bottom flask with stirring. Then, 15.89 g of ethyl vinyl ether (52.9 mL) was added to the solution with stirring. The solution was heated at 80 °C overnight under N₂. Upon cooling, the deeply colored precipitate was filtered and dried. The yield was 90%.

**Synthesis of the BIP Mediator.** This synthesis was carried out in five steps.

1. Synthesis of 3,5-di-tert-butyl-2-hydroxybenzaldehyde. Commercially available 2,4-di-tert-butylphenol (10.0 g, 48.5 mmol, 1 equiv.) and hexamethylenetetramine (13.6 g, 97.0 mmol, 2 equiv.) were dissolved in trifluoroacetic acid (40 mL), and the mixture was heated at reflux for 6 h. The reaction was quenched with hot with a 33% (vol/vol) aqueous H₂SO₄ solution (40 mL). The resulting mixture was allowed to cool to room temperature while stirring. The crude product was extracted with diethyl ether (3 × 50 mL), and the extract was neutralized with a saturated aqueous solution of sodium bicarbonate (2 × 100 mL), then washed with water (3 × 100 mL). The organic phase was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO₂) using hexanes/EtOAc (9:1, v/v) as the eluent to afford the title compound as a colorless solid in a 35% yield (4.0 g).

$^1$H NMR (400 MHz, CDCl₃, 6 ppm): 11.65 (s, 1H, CHO); 9.86 (s, 1H, CHO); 7.60 (d, J = 1.7 Hz, 1H, H₆); 7.36 (d, J = 1.7 Hz, 1H, H₅); 1.46 (s, 9H, Bu₃); 1.36 (s, 9H, Bu₃). 

C NMR (400 MHz, CDCl₃, 6 ppm): 191.5; 154.8; 138.4; 138.1; 131.2; 128.3; 123.9; 34.5; 31.2; 31.0. MALDI-TOF (positive mode, cyano-4-hydroxycinamic acid as matrix): m/z 235.04 (M + H)⁺ (100 %), calculated 234.20 for C₁₈H₂O₂.

2. Synthesis of 2-(3′,5′-di-tert-butyl-2-hydroxyphenyl)-5-carboxymethoxybenzimidazole. Phenyl 3,5-di-tert-butyl-2-hydroxybenzoate (1.5 g, 6.41 mmol) in nitrobenzene (10 mL) was added dropwise to a suspension of methyl 3,4-diaminobenzoate (1.06 g, 6.41 mmol) in nitrobenzene (10 mL). The mixture was heated at reflux (210 °C) in a sand bath for 12 h under an inert atmosphere. After cooling, and without any workup, the crude mixture was applied to a chromatography column (SiO₂, in hexanes) and nitrobenzene was eluted with a mixture of hexanes/ethyl acetate (95:15, v/v). The target compound was then eluted with a hexanes/ethyl acetate (85:15, vol/vol) mixture as a light orange solid (2.18 g, 89% yield).

$^1$H NMR (400 MHz, CDCl₃, 5 ppm) two tautomers: 13.42 (br, 1H, NH); 11.03 (s, 0.5 H, NH); 10.86 (s, 0.5 H, NH); 8.41 (s, 0.5 H, H₆); 8.13 (s, 0.5 H, H₅); 7.97 (d, J = 8.0 Hz, 0.5 H, H₆); 7.92 (d, J = 8.0 Hz, 0.5 H, H₅); 7.68 (d, J = 8.0 Hz, 0.5 H, H₆); 7.64 (s, 0.5 H, H₅); 7.59 (s, 0.5 H, H₆); 7.48 (s, 1 H, H₃); 7.29 (d, J = 8.0 Hz, 0.5 H, H₉); 3.96 and 3.89 (s, 3H, COOCH₃); 1.54 (s, 9H, Bu₃); 1.34 and 1.27 (s, 9H, Bu₃). MALDI-TOF (positive mode, cyano-4-hydroxycinamic acid as matrix): m/z 381.21 (M + H)⁺ (100 %), calculated 380.20 for C₂₃H₂₂N₂O₃.

3. Synthesis of 2-(3′,5′-di-tert-butyl-2-hydroxyphenyl)-5-methylhydroxybenzimidazole. Note: For this reaction, tetrahydrofuran was freshly distilled from sodium/benzophenone. Sodium and lithium aluminum hydride are highly flammable and react violently with water. The authors strongly recommend the use of appropriate protective equipment while performing the protocol described in the following.

A solution of 5-carboxymethoxy-2-(3′,5′-di-tert-butyl-2-hydroxyphenyl)benzimidazole (2.00 g, 5.26 mmol) in tetrahydrofuran (25 mL) was added dropwise over a period of ten min to a cooled suspension (ethanol/liquid nitrogen bath, −78 °C) of lithium aluminum hydride (4.00 g, 10.52 mmol) in tetrahydrofuran (25 mL). Upon completion of the addition, the mixture was allowed to warm to room temperature and stirred for 3 h. The reaction flask was then cooled back to −78 °C and
quenched with the dropwise addition of ethanol (25 mL) followed by dropwise addition of water (5 mL). The mixture was allowed to warm to ambient temperature and then filtered through paper, and the solvents were evaporated under reduced pressure. The crude product was dissolved in ether (100 mL) and washed with water (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. The residue was recrystallized from dichloromethane/hexanes to yield the target compound as a white solid in 97% yield (1.8 g). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 6 ppm), two tautomers: 13.41 (brs, 1H, OH); 9.61 (brs, 0.5 H, NH\textsubscript{1}); 9.45 (brs, 0.5 H, NH\textsubscript{2}); 7.71 (brs, 0.5 H, H\textsubscript{1}); 7.68 (s, 0.5 H, H\textsubscript{2}); 7.52 (d, J = 8.6 Hz, 0.5 H, H\textsubscript{3}); 7.48-7.44 (m, 1.5 H, H\textsubscript{4}, H\textsubscript{5}, and H\textsubscript{6}); 7.43 (brd, J = 2.0 Hz, 0.5 H, H\textsubscript{7}); 7.40 (brd, J = 2.0 Hz, 0.5 H, H\textsubscript{8}); 7.31 (brd, J = 8.6 Hz, 0.5 H, H\textsubscript{9}); 7.28 (brd, J = 8.6 Hz, 0.5 H, H\textsubscript{10}); 4.21 (s, 2H, CH\textsubscript{2}OH); 1.51 (s, 9H, Bu\textsubscript{1}); 1.38 (s, 9H, Bu\textsubscript{2}); MALDI-TOF (positive mode, cyano-4-hydroxyquinic acid as the matrix): \textit{m/z} 353.22 (M + H\textsuperscript{+}) (100%), calculated 352.20 for C\textsb{12}H\textsb{18}N\textsb{2}O\textsb{2}.


Activated manganese dioxide (3.58 g, 41.25 mmol) was added to a solution of 2-(3′,5′-di-tert-butyl-2′-hydroxyphenyl)-5-methylhydroxymidazolide (1.45 g, 4.12 mmol) in dichloromethane (150 mL). The mixture was stirred for 5 h at room temperature. The crude suspension was filtered through paper, and then it was concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO\textsubscript{2}) using a mixture of hexanes/ethyl acetate (90:10, vol/vol) as eluent to afford the title compound as a yellow solid in 85% yield (1.22 g). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 6 ppm): 13.30 (brs, 0.5 H, OH); 13.19 (brs, 0.5 H, OH); 11.00 (brs, 0.5 H, NH\textsubscript{1}); 10.80 (brs, 0.5 H, NH\textsubscript{2}); 10.06 (s, 1H CH\textsubscript{2}OH); 8.21 (d, J = 8.4 Hz, 1H, H\textsubscript{1}); 7.81 (s, 2H, H\textsubscript{2} and H\textsubscript{3}); 7.66 (d, J = 8.4 Hz, 1H, H\textsubscript{4}); 7.50 (s, 1H, H\textsubscript{5}); 1.51 (s, 9H, Bu\textsubscript{1}); 1.36 (s, 9H, Bu\textsubscript{2}); MALDI-TOF (positive mode, cyano-4-hydroxyquinic acid as matrix): \textit{m/z} 353.22 (M + H\textsuperscript{+}) (100%), calculated 352.20 for C\textsb{12}H\textsb{18}N\textsb{2}O\textsb{2}.

5. Synthesis of diethyl 2-(2-(3,5-di-tert-butyl-2-hydroxyphenyl)-1H-benzo[d]imidazol-5-yl)methane). To a solution of 2-(3′,5′-di-tert-butyl-2′-hydroxyphenyl)-5-formylbenzimidazolide (1.02 g, 2.92 mmol) in toluene (250 mL) was added diethyl malonate (1.168 g, 11.7 mL, 7.30 mmol), piperidine (0.297 g, 0.35 mL, 3.50 mmol), and acetic acid (0.183 g, 0.175 mL, 3.50 mmol). The reaction mixture was heated at reflux with a Dean-Stark distilling trap for 24 h. The reaction mixture was concentrated under reduced pressure, and the final purification was achieved by column chromatography (SiO\textsubscript{2}) using a mixture of hexanes/ethyl acetate (90:10, vol/vol) as eluent to afford the title compound as a yellow solid in 72% yield (1.09 g). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 6 ppm), two tautomers: 13.28 (s, 1H, OH); 10.32 (s, 0.5 H, NH\textsubscript{1}); 10.27 (s, 0.5 H, NH\textsubscript{2}); 7.74 (s, 0.5 H, ArH); 7.70 (s, 0.5 H, ArH); 7.65 (s, 0.5H, ArH); 7.49 (d, J = 8.0 Hz, 0.5 H, ArH); 7.43 (m, 1H, ArH); 7.38 (m, 1H, ArH); 7.31 (s, 0.5 H, ArH); 7.17 (m, 1H, ArH); 7.12 (d, 0.5 H, ArH) 4.31 (m, 2H, CH\textsubscript{2}); 4.21 (m, 2H, CH\textsubscript{2}); 1.54 (s, 9H, Bu\textsubscript{1}); 1.29 (s, 9H, Bu\textsubscript{2}); 1.20 (m, 6H, CH\textsubscript{2}); MALDI-TOF (positive mode, cyano-4-hydroxyquinic acid as matrix): \textit{m/z} 493.19 (M + H\textsuperscript{+}) (100%), calculated 492.3 for C\textsb{29}H\textsb{36}N\textsb{2}O\textsb{5}.

Electrochemical Determination of Current Efficiency. Following a previously reported procedure (1), a pseudo Clark electrode was held in close proximity to the TiO\textsubscript{2} electrode to collect photoelectrochemically generated oxygen. An 80% collection efficiency Pt electrode was calibrated at –490 mV vs Ag/AgCl (this potential was chosen to maximize the oxygen collection efficiency while minimizing the current from hydrogen evolution) to reduce the oxygen generated from a facing Pt electrode held at +1200 mV vs Ag/AgCl. The measurements were taken in 37.5 mM Na\textsb{3}SiF\textsb{6}-NaHCO\textsb{3} (1:1.5) silicate buffer (pH 5.8) containing 0.1 M LiClO\textsubscript{4} as the supporting electrolyte under a blanket of Ar gas. The calibrated collecting electrode was then assembled with the photoelectrode, in the same configuration as the Pt generator electrode, and then it was connected to the biopotentiostat. The photoelectrode and Pt collector electrode were held at 0 mV and –490 mV vs Ag/AgCl, respectively. The Faradic efficiency of oxygen generation was calculated to be 87% and 86% for 3P-Ru dye +1-IrO\textsb{2}, nH\textsb{2}O (Fig. S2-A) and 3P-Ru dye +2-IrO\textsb{2}, nH\textsb{2}O (Fig. S2B), respectively.

Fig. S1. $^1$H NMR spectrum of 3P-Ru.

Fig. S2. $^1$H NMR spectrum of 3,5-di-tert-butyl-2-hydroxybenzaldehyde, 400 MHz, CDCl$_3$, 25 °C.
Fig. S3. $^1$H NMR spectrum of 2-(3′,5′-di-tert-butyl-2′hydroxyphenyl)-5-carbomethoxybenzimidazole, 400 MHz, CDCl$_3$, 25 °C.
Fig. S4. $^1$H NMR spectrum of the target compound, 400 MHz, CDCl$_3$, 25 °C.
Fig. S5. $^1$H NMR spectrum of the target compound, 400 MHz, CD$_3$OD, 25 °C.

Fig. S6. Cyclic voltammograms showing the first oxidation of benzimidazole-phenol mediator (black) and a scan, after the addition of ferrocene (gray). The midpoint potential for the oxidation of the benzimidazole-phenol occurs at 1.06 V vs. SCE with a peak separation of 70 mV.
Fig. S7. Generator-collector current measurements with illuminated TiCl$_4$-treated TiO$_2$ photoelectrodes sensitized by (A) 3P-Ru dye $+$ 1-IrO$_x$ $\cdot$ nH$_2$O nanoparticles (2.3 cm$^2$) and (B) 3P-Ru dye $+$ 2-IrO$_x$ $\cdot$ nH$_2$O nanoparticles (1.8 cm$^2$) at 0 mV vs. Ag/AgCl, with the Pt collector electrode at $-490$ mV vs. Ag/AgCl.

Scheme S1. Synthesis of 3P-Ru dye.